

Quantifying PM_{2.5} Source Contributions for the San Joaquin Valley with Multivariate Receptor Models

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UNMIX and Positive Matrix Factorization (PMF) solutions to the Chemical Mass Balance (CMB) equations were applied to chemically speciated PM_{2.5} measurements from 23 sites in California's San Joaquin Valley to estimate source contributions. Six and seven factors were determined by UNMIX for the low_PM_{2.5} period (February to October) and high_PM_{2.5} period (November to January), respectively. PMF resolved eight factors for each period that corresponded with the UNMIX factors in chemical profiles and time series. These factors are attributed to marine sea salt, fugitive dust, agriculture—dairy, cooking, secondary aerosol, motor vehicle, and residential wood combustion (RWC) emissions, with secondary aerosol and RWC accounting for over 70% of PM_{2.5} mass during the high_PM_{2.5} period. A zinc factor was only resolved by PMF. The contribution from motor vehicles was between 10 and 25% with higher percentages occurring in summer. The PMF model was further evaluated by examining (1) site-specific residuals between the measured and calculated concentrations, (2) comparability of motor vehicle and RWC factors against source profiles obtained from recent emission tests, (3) edges in bi-plots of key indicator species, and (4) spatiotemporal variations of the factors' strengths. These evaluations support the compliance with model assumptions and give a higher confidence level to source apportionment results for the high_PM_{2.5} period.

Introduction

Persistent high particulate matter (PM) concentrations in California's San Joaquin Valley (SV) (1, 2) stimulated initiation of the California Regional PM₁₀/PM_{2.5} Air Quality Study (CRPAQS) (3), and the associated Fresno Supersite (4), to identify the causes of elevated PM levels and to evaluate means for remediation. An important CRPAQS objective is to quantify source contributions to annual and high PM concentrations.

Presented here are results from the Positive Matrix Factorization (PMF) and UNMIX solutions to the Chemical Mass Balance (CMB) equations (5) for PM_{2.5} (PM with aerodynamic diameter <2.5 μm) source apportionment. These results can be compared with the single-sample

effective variance solution (6) to the CMB equations and/or source contribution estimates from source-oriented models so that a "weight of evidence" approach can be used to develop cost-effective control strategies (7). Owing to the special topography and meteorology of the SV and the predominance of area and mobile emissions, urban and rural sites are influenced by similar sources, but by differing amounts. This allows the application of receptor models to multiple-site measurements over seasonal monitoring periods during which the emission rates and source profiles are reasonably constant. This analysis (1) demonstrates the applicability of PMF and UNMIX to spatially as well as temporally distributed measurements, and (2) evaluates the consistency and reliability of PMF and UNMIX solutions in preparation for comparison with other receptor- and source-oriented models.

Methods

Ambient Observations. The CRPAQS ambient network covered a region ~600 km long by 200 km wide between Bodega Bay on the northwest California Coast and Edwards Air Force Base in the Mojave Desert (Figure 1). Site characteristics and measured parameters are described in the Supporting Information (Table S-1) and Chow et al. (3). 24-Hour sampling based on the U.S. EPA sixth-day compliance schedule was carried out from 12/2/1999 to 2/3/2001. During the winter of 2000–2001, intensive observation periods (IOPs) obtained speciated PM_{2.5} measurements five times a day in the urban areas of Fresno (FSF) and Bakersfield (BAC) and at non-urban Angiola (ANGI), Bethel Island (BTI), and Sierra Nevada Foothills (SNFH) sites on 15 days selected by forecast (3). Most sites reported >90% data recovery between 1/1/2000 and 1/31/2001.

Chow et al. (3) and Rinehart et al. (8) describe the PM_{2.5} spatiotemporal characteristics. PM_{2.5} concentrations varied with elevation. While the valley floor experienced annual PM_{2.5} up to 30 μg/m³, concentrations generally decreased to <5 μg/m³ at the surrounding coastal, mountain, and desert monitors. For non-urban sites in the SV, elevated PM_{2.5} in late fall and winter was mostly driven by ammonium nitrate (NH₄NO₃), while carbonaceous material exacerbated PM_{2.5} pollution in urban areas such as Modesto (M14), Visalia (VCS), Fresno (FSF), and Bakersfield (BAC). Regional transport occurs aloft at night through a valley-wide layer that is decoupled from a shallow (20–30 m) nighttime surface layer during winter (2) and through a well-defined daytime northwest-to-southeast flow during non-winter periods (9).

Based on these analyses, CRPAQS samples have been divided into low_PM_{2.5} (February to October) and high_PM_{2.5} (November to January) periods (3) that approximately correspond to the winter and non-winter emissions and climatological regimes. The high_PM_{2.5} period contributed 50–75% of annual PM_{2.5} at within-valley sites (lower elevation) with the highest contributions found in the urban areas. For three desert sites outside the SV—China Lake (CHL), Mojave (MOP), and Olancho (OLW)—the high_PM_{2.5} period contribution was <25% of the annual average, consistent with a limited transport from the SV to the Mojave Desert during winter.

Multivariate Receptor Models. UNMIX (10, 11) and PMF (12, 13) solve the CMB equations and are therefore subject to the same derivation of CMB from physical principles with its underlying assumptions. C_{it} , the concentration of the i^{th} chemical species measured at time or location t , is the linear

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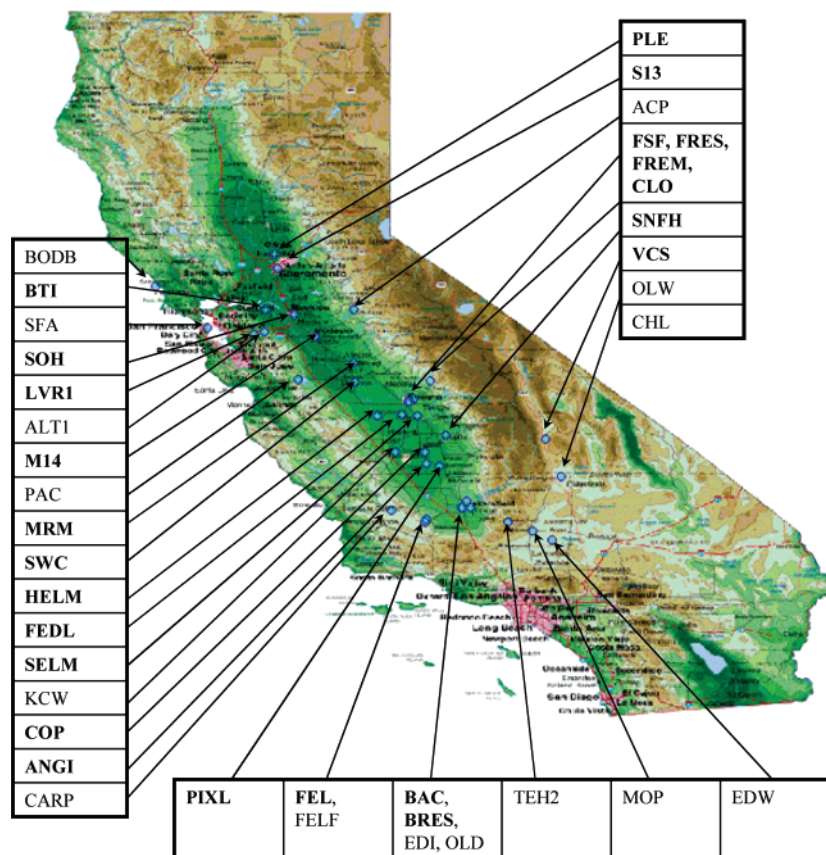


FIGURE 1. Ambient PM_{2.5} sampling network for CRPAQS. Sites in bold are included in this study. (ACP: Angels Camp; ALT1: Altamont Pass; ANGI: Angiola; BAC: Bakersfield; BODG: Bodega Marine Lab; BRES: Bakersfield Residential; BTI: Bethel Island; CARP: Carrizo Plain; CHL: China Lake; CLO: Clovis; COP: Corcoran; EDI: Edison; EDW: Edwards Air Force Base; FEDL: Dairy; FEL: Fellows; FELF: Foothills above Fellows; FRES: Fresno Residential; FSF: Fresno; HELM: Helm-Central Fresno County; KCW: Kettleman City; LVRI: Livermore; M14: Modesto; MOP: Mojave-Poole; MRM: Merced; OLD: Oildale-Manor; OLW: Olancha; PAC: Pacheco Pass; PIXL: Pixley Wildlife Refuge; PLE: Pleasant Grove; S13: Sacramento; SELM: Selma; SFA: San Francisco; SNFH: Sierra Nevada Foothills; SOH: Stockton-Hazelton; SWC: Southwest Chowchilla; TEH2: Tehachapi Pass; VCS: Visalia Church St.).

sum of contributions from a number of independent sources or factors:

$$C_{it} = \sum_j F_{ij} S_{jt} + E_{it} \quad (1)$$

F_{ij} is the fractional abundance of the i^{th} species in the j^{th} source type, S_{jt} is the normalized contribution of the j^{th} source at time and/or location t , and E_{it} represents the error between the measured and calculated ambient concentrations.

Receptor models such as PMF and UNMIX estimate F_{ij} and S_{jt} by minimizing:

$$Q \text{ or } \chi^2 = \sum_i \sum_t [E_{it}/\sigma_{it}]^2 = \sum_i \sum_t [(C_{it} - \sum_j F_{ij} S_{jt})/\sigma_{it}]^2 \quad (2)$$

where the weighting factor, σ_{it} , intends to represent the magnitude of E_{it} . Although ambient measurement precisions are often used for σ_{it} (as in this study), this is an underestimation as most of the uncertainty originates from variability in the emissions (6). UNMIX and PMF limit solutions of eq 2 to nonnegative F_{ij} and S_{jt} . The resolved UNMIX and PMF factors should be associated with emission sources by comparing the F_{ij} with measured source profiles.

When C_{it} are available from several times and locations, it is possible to expand eq 1 to a three-way factor analysis (14, 15). Such analyses contain a large number of factors and often require additional constraints to stabilize the solutions. Source emissions are also assumed to be reasonably similar for the range of sample times and locations.

UNMIX v2.3 software applied in this study limits itself to seven factors, while a newer version (UNMIX v5, currently in beta testing) sets no limit. These UNMIX v2.3 results are equivalent to those obtained from the beta version. EPA PMF v1.1 (16) software was applied because it selects random initial points for multiple runs and allows bootstrap testing to evaluate the uncertainty of rotational freedom (17). When running in a robust mode, PMF adapts the Huber influence function, a technique for iterative reweighting of the input data values to lessen the influence of extreme values (18).

UNMIX and PMF have been previously applied to many PM_{2.5} source apportionment studies (19–24), but their results do not always agree (23, 24). Differences are attributed to the following: (1) different strategies for treating uncertainties and seeking the best fit; (2) different constraints on factor rotational freedom; and (3) different practitioner preferences. Applying both models to the same measurements and reconciling their source contribution estimates with each other and source-oriented models (e.g., 25) provides the basis for the weight of evidence approach.

Source and Receptor Characteristics. Potential sources of PM_{2.5} in the SJV are summarized in the Supporting Information along with expected chemical markers. For California, area sources, including road/fugitive dust, residential and agriculture burning, construction, and cooking, account for about 76% of primary statewide PM_{2.5} emissions (Table S-2). Approximately half of the remaining directly emitted PM_{2.5} (12%) originates from on-road and off-road engine exhaust. Source activities are spatially inhomogeneous but, as noted earlier, mixing within the SJV takes place within

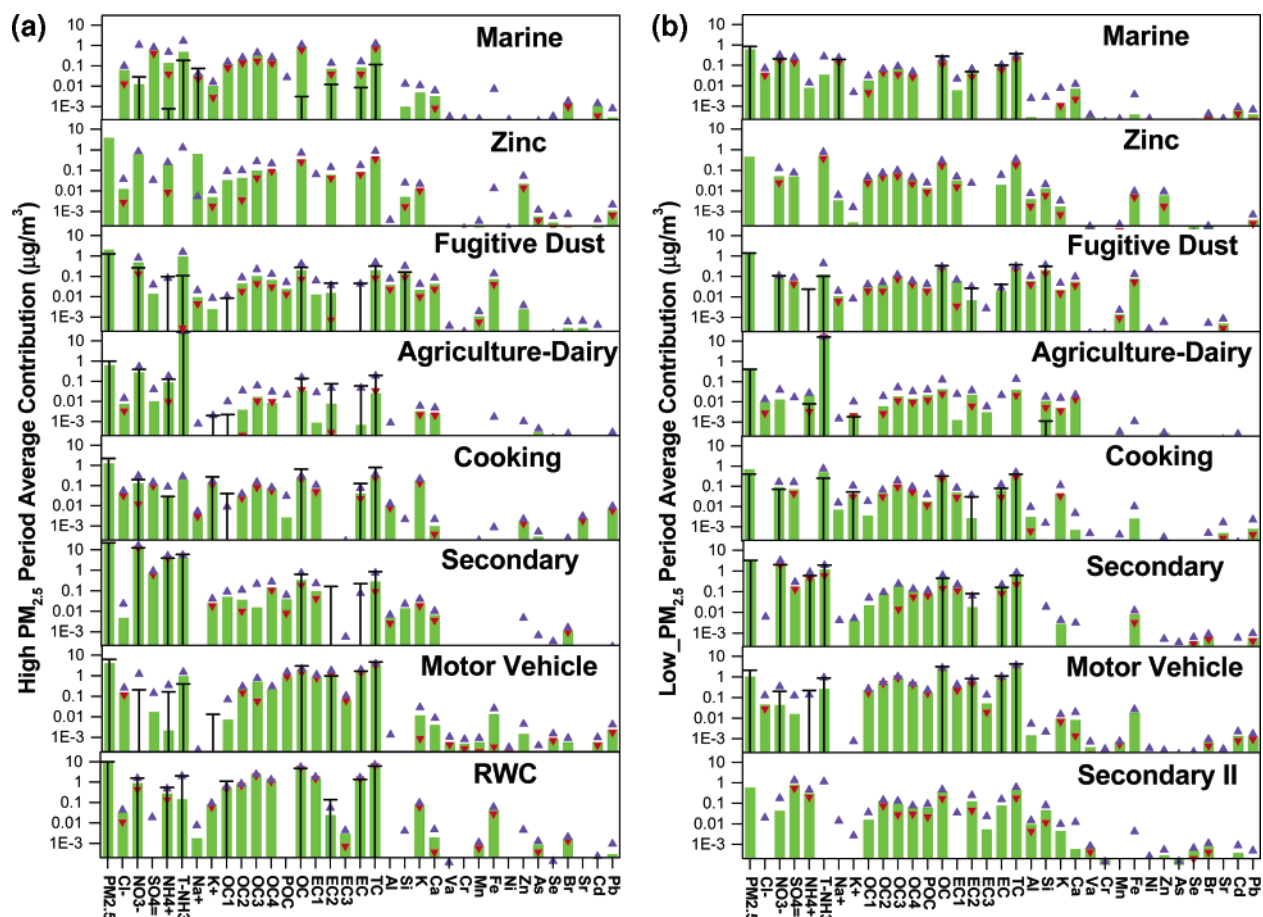


FIGURE 2. UNMIX (vertical lines) and PMF (bars) factor profiles for (a) high_ $PM_{2.5}$ and (b) low_ $PM_{2.5}$ periods, in terms of average contributions to $PM_{2.5}$ mass and fitting species. The upper and lower triangles represent the upper and lower bounds of the PMF factor contribution, respectively, determined from the 95th and 5th percentile bootstrapping values. RWC = residential wood combustion.

a day during summer and over a few days during winter (2, 3, 9).

Each site had from 46 to 76 days of speciated $PM_{2.5}$ measurements (Table S-3). Though PMF and UNMIX do not specify a minimum number of samples, the stability of their solutions increases with the number of samples. The sample sets must have a large variation in source contributions among different samples, and the chemical profiles of the contributing sources should remain constant within a source type but differ substantially between source types. The CRPAQS $PM_{2.5}$ dataset meets these requirements because area and mobile source profiles are reasonably consistent, in the aggregate, throughout the SJV (i.e., not site-specific); and there is a large expected variability between source contributions by sampling time and location (26).

Mineral processing, gas-fired electricity production, oil and gas extraction, and agricultural processing are important stationary sources in central California, but their primary $PM_{2.5}$ emission rates are small compared to those of area and mobile sources (Table S-2). Some CRPAQS sites were located within or next to dairies (FEDL), oilfields (FEL), and agricultural operations (HELM). PMF and UNMIX are expected to identify profiles of these specific sources and estimate much higher contributions from them at the nearby locations than at more distant receptors. This situation is analogous to these and other factor models identifying a fireworks factor that only contributes on the Fourth of July (e.g., 27).

Emission factors and chemical profiles of the area and mobile sources are expected to differ between seasons. Motor vehicle cold starts are more prevalent during the winter season. Wood stoves and fireplaces are only used during

TABLE 1. Fractional Contributions of UNMIX and PMF Factors to Valleywide $PM_{2.5}$ during Winter and Non-Winter Periods

factors	high_ $PM_{2.5}$ (Nov. – Jan.)		low_ $PM_{2.5}$ (Feb. – Oct.)	
	UNMIX	PMF	UNMIX	PMF
marine	0%	0%	10%	7%
fugitive dust	3%	5%	16%	19%
agriculture–dairy	2%	2%	5%	4%
cooking	5%	3%	5%	9%
secondary aerosol	51%	48%	38%	36%
motor vehicle	15%	10%	25%	13%
residential wood combustion	24%	23%		
secondary aerosol II				7%
zinc		9%		6%

winter, while agricultural burning and wildfires are more prevalent during warm non-winter periods. The large change of temperature and relative humidity from summer to winter alters the thermodynamic equilibrium between particle-phase and gas-phase pollutants and possibly modifies the factors representing secondary aerosol composed of NH_4 – NO_3 , ammonium sulfate $[(NH_4)_2SO_4]$, and organic matter. To ensure uniformity of source profiles, the UNMIX and PMF analyses were limited to 23 “within-valley” sites identified in Figure 1. The low_ $PM_{2.5}$ and high_ $PM_{2.5}$ periods that contain a total of 929 and 670 samples, respectively, were analyzed separately.

Results and Discussion

Magliano et al. (28) used a nine-source single-sample effective variance solution to explain 81–91% of winter 1995 $PM_{2.5}$ in

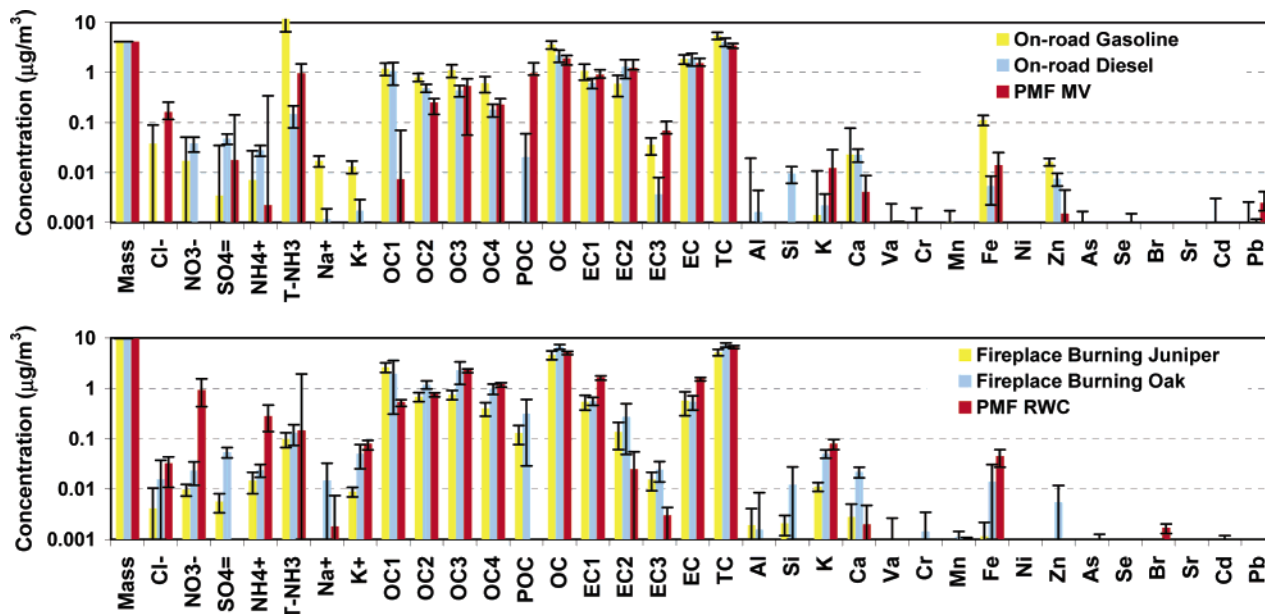


FIGURE 3. Comparisons of PMF motor vehicle (MV) and residential wood combustion (RWC) factors with measured source profiles (normalized to average source contributions during CRPAQS). The uncertainties of PMF factors are those in Figure 2 while the uncertainties in measured profiles are determined from the standard deviation of averages from different emitters within the source type.

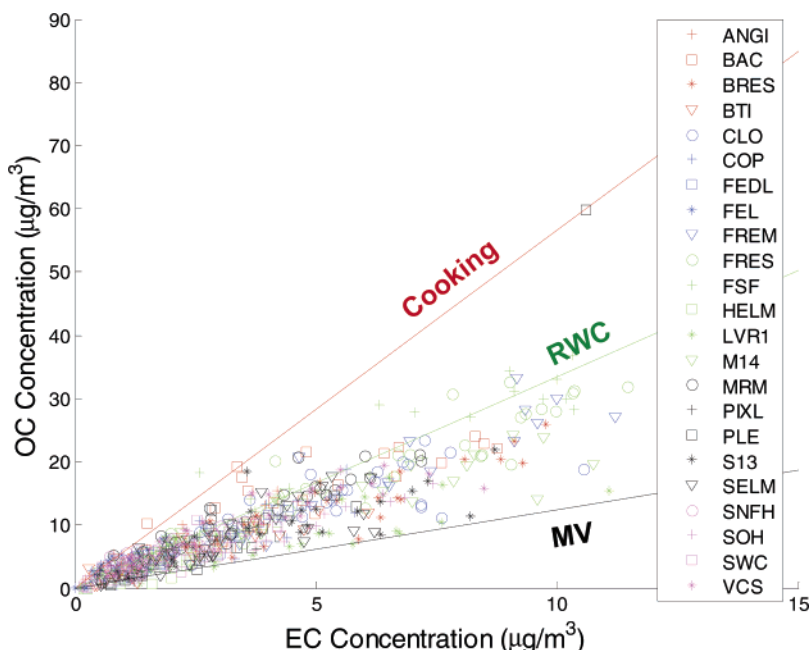


FIGURE 4. OC versus EC for all samples and by site collected during the high_{PM_{2.5}} period. Solid lines indicate the OC/EC ratios in the MV, RWC, and cooking PMF factors.

the SJV. Source types included two geological (i.e., road dust and construction), three secondary aerosol (i.e., NH_4NO_3 , $(\text{NH}_4)_2\text{SO}_4$, OC), vegetative burning, vehicle exhaust, industry (oilfield), and marine emitters. Industry and construction contributed minor fractions ($<0.1\%$) at urban and rural sites. Schauer and Cass (29) estimated similar source contributions for multi-day composites during winter 1995, using organic markers, but they resolved the motor vehicle portions into gasoline and diesel contributions and the vegetative burning portions into hardwood, softwood, and cooking contributions.

UNMIX and PMF Analysis. $\text{PM}_{2.5}$ mass was not used as input to either model to obtain factors, but it was used to apportion $\text{PM}_{2.5}$ to the factors. Initial UNMIX trials used nitrate (NO_3^-), sulfate (SO_4^{2-}), ammonium (NH_4^+), ammonia (NH_3), soluble sodium (Na^+), soluble potassium (K^+), organic

carbon (OC), elemental carbon (EC), total carbon (TC), thermal carbon fractions (OC1–OC4, OP, and EC1–EC3 quantified by the IMPROVE_TOR protocol (30)), and silicon (Si) measurements. Na^+ , K^+ , and Si are the indicators for marine air intrusion, vegetative burning, and fugitive dust, respectively. High-temperature EC (EC2, EC fraction evolved at 700°C in an oxidative environment) dominates the PM emission from diesel engines but is a minor component of gasoline emission and wood smoke (31, 32). Although $>80\%$ of the variability in both high_{PM_{2.5}} and low_{PM_{2.5}} samples would be explained by seven principle components, no feasible solutions were found by UNMIX. By applying the UNMIX “OVERNIGHT” option to evaluate all possible combinations, 6-factor and a 7-factor solutions were found for the low_{PM_{2.5}} and high_{PM_{2.5}} periods, respectively, using common species NO_3^- , NH_4^+ , total ammonium ($\text{T-NH}_3 =$

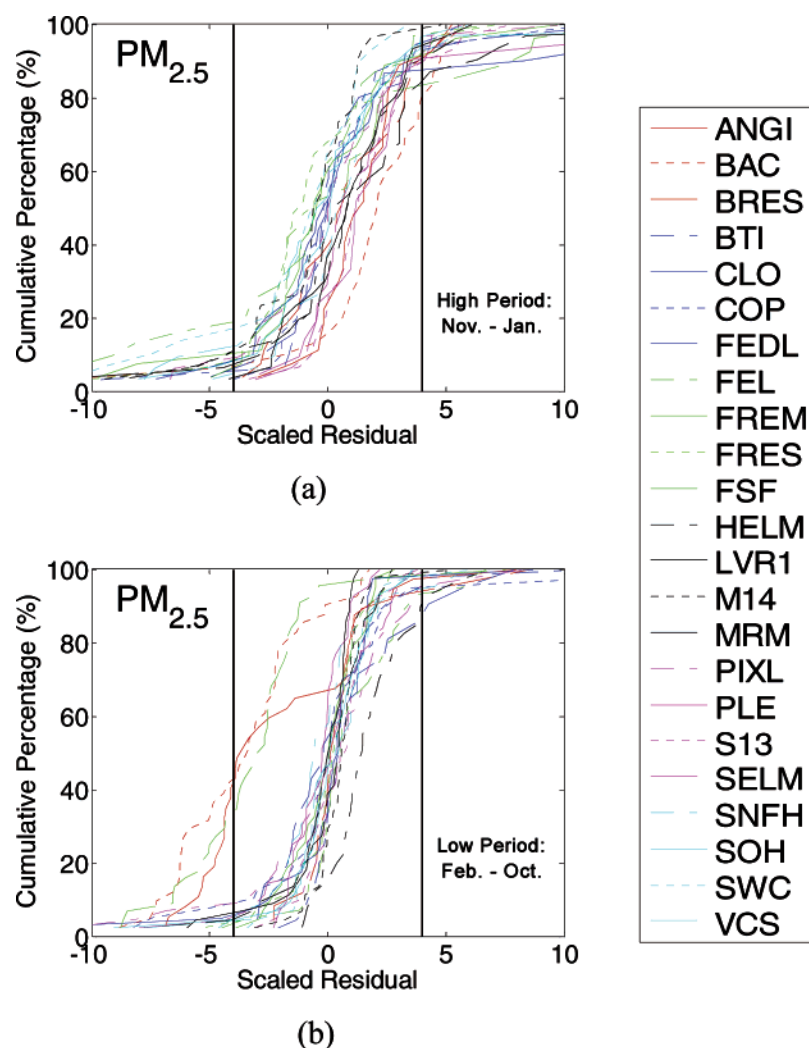


FIGURE 5. Cumulative PMF scaled residuals (difference between calculated and measured $\text{PM}_{2.5}$), by site, for the high- $\text{PM}_{2.5}$ and low- $\text{PM}_{2.5}$ periods. The vertical lines indicate scaled residuals of ± 4 ; i.e., the difference between calculated concentration from the measured value is four times the measurement uncertainty.

$\text{NH}_3 + \text{NH}_4^+$), Na^+ , K^+ , OC, EC2, EC, TC, and Si, and an additional species OC1 for the high- $\text{PM}_{2.5}$ period only. Signal/noise ratios and strengths in both solutions were ~ 2 or higher.

PMF included 27 species that were above lower quantifiable limits (LQL) for at least 50% of the samples plus the eight thermal carbon fractions (Table S-3). Eight-factor solutions were determined by PMF with the robust mode for both the high- and low- $\text{PM}_{2.5}$ periods. FPEAK and FKEY are often adjusted to rotate PMF factors toward known source profiles or contributions (e.g., 33, 34). EPA PMF v1.1 software does not contain FPEAK or FKEY options, but the uncertainty in PMF solutions can be estimated using a bootstrapping technique coupled with a method to account for rotational freedom (16). Figure 2 presents the PMF factors with upper and lower bounds determined from the 5th and 95th percentiles of 100 bootstrap values. The median Q values were 20 858 (low- $\text{PM}_{2.5}$ period) and 18 964 (high- $\text{PM}_{2.5}$ period), compared to ideal values of 31 586 (low- $\text{PM}_{2.5}$ period) and 22 780 (high- $\text{PM}_{2.5}$ period). The ideal Q is the number of measured C_{it} , assuming that the model contains only measurement uncertainty that has been accurately determined (i.e., $E_{it}/\sigma_{it} = 1$). The Q analysis implied seven or eight factors for both periods. Eight-factor models were selected for a better comparison of their profiles with UNMIX factors and measured source profiles from recent emission tests.

The contribution of each factor to $\text{PM}_{2.5}$ was estimated by an unweighted multiple linear regression with zero intercept

against the factor scores (S_{ji}) (e.g., 35, 36). The regression correlations were high; $r = 0.92$ (UNMIX)/0.96 (PMF) and 0.79- (UNMIX)/0.87 (PMF) for the high- and low- $\text{PM}_{2.5}$ period, respectively. The UNMIX factors were paired with the PMF factors by ranking correlations of each of the UNMIX factors with each of the PMF factors in time series. Each UNMIX factor correlated well (e.g., $r > 0.8$ for most cases) with one and only one PMF factor (Table S-4), so there was no ambiguity in matching the pairs. Figure 2 compares the UNMIX and PMF factors. Their common species agree within the PMF bootstrap uncertainties.

Based on source markers, seven common factors resolved by UNMIX and PMF for the high $\text{PM}_{2.5}$ period are (1) marine (Na^+); (2) fugitive dust (Si); (3) agriculture-dairy (T- NH_3 , OC); (4) cooking (K^+ , OC, EC); (5) secondary aerosol (NO_3^- , NH_4^+ , OC); (6) motor vehicle (OC, EC2, EC); and (7) residential wood combustion (K^+ , Cl^- , OC1, OC, EC). The extra factor from PMF contains a high zinc (Zn) content and could be related to brake and tire wear (37). For the low- $\text{PM}_{2.5}$ period, the six common factors are (1) marine; (2) fugitive dust; (3) agriculture-dairy; (4) cooking; (5) secondary aerosol; and (6) motor vehicle exhaust. The additional two factors from PMF are Zn and another secondary aerosol factor featuring $(\text{NH}_4)_2\text{SO}_4$.

Larger discrepancies between the UNMIX and PMF profiles occur for the marine factor during the high- $\text{PM}_{2.5}$ period (Figure 2a), but neither model apportions $\text{PM}_{2.5}$ mass

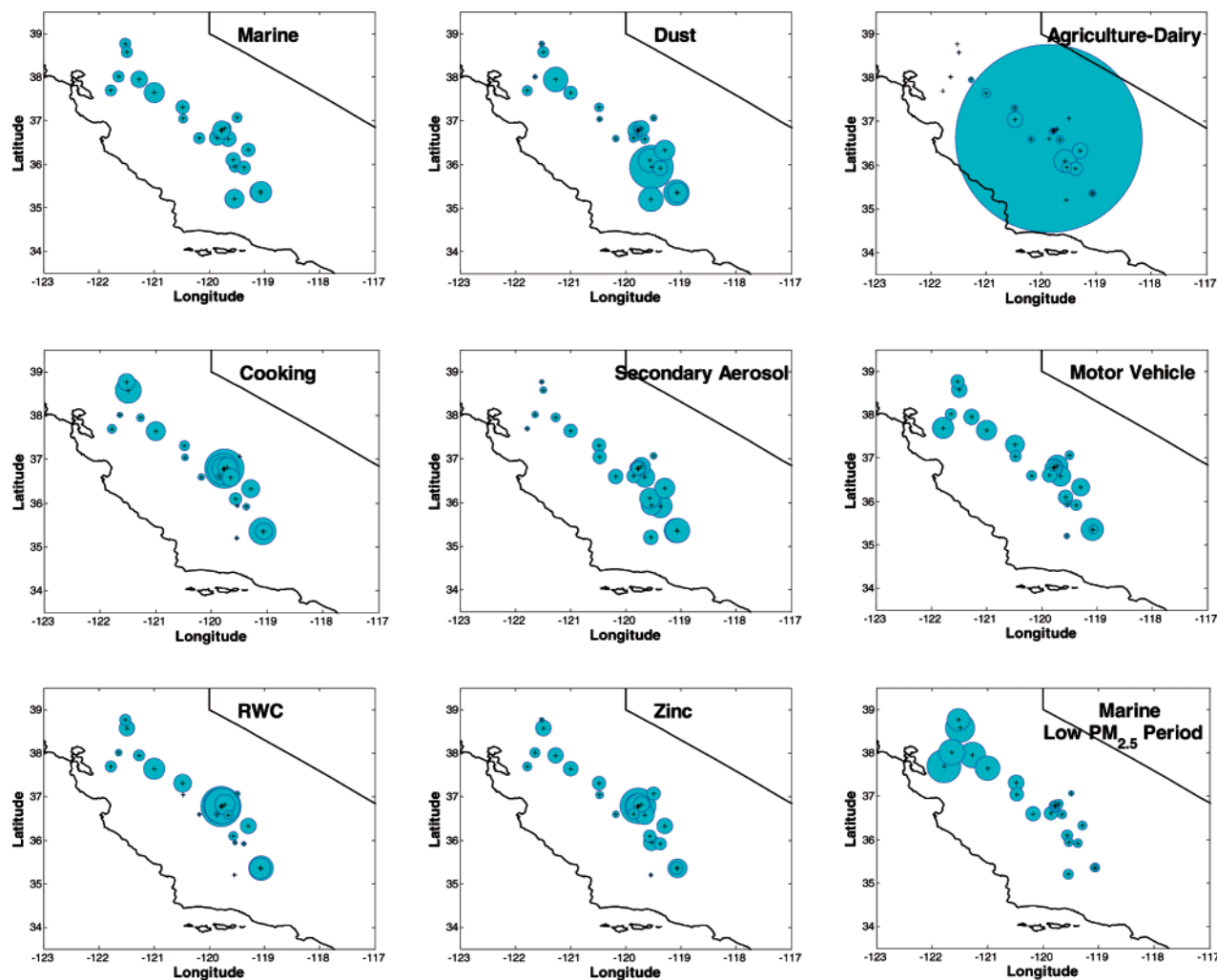


FIGURE 6. Spatial distributions of temporally averaged PMF factor contribution estimates for the high_{PM_{2.5}} period (Nov.–Jan.). The distribution of marine factor during the low_{PM_{2.5}} period is also presented (last panel).

to this factor. PMF consistently allocates carbon and silicon to the agriculture–dairy factor for the low_{PM_{2.5}} period, while UNMIX does not. Contribution estimates for these minor factors may contain higher uncertainties. The residential wood combustion (RWC) factor appears only during the wintertime high_{PM_{2.5}} period, and the sulfate factor appears only during the non-winter low_{PM_{2.5}} period. This is consistent with the expected seasonal variations of these sources; i.e., residential heating demand increases during the winter while sulfate is more efficiently formed during summer. The OC/EC ratio in the motor vehicle (MV) factor is lower (1.2 by PMF and 1.7 by UNMIX) for the high_{PM_{2.5}} period than for the low_{PM_{2.5}} period (2.8 by both PMF and UNMIX. Cadle et al. (38) report a similar seasonal trend of OC/EC ratio for Denver, CO.

Annual average PM_{2.5} concentrations are well explained within $\pm 1\%$ by both UNMIX and PMF factors (Table 1). Secondary aerosol, RWC, and vehicle contributions account for $\sim 90\%$ of the PM_{2.5} mass during the high_{PM_{2.5}} period if the Zn factor is classified as a mobile source contribution. UNMIX and PMF achieve similar source contribution estimates and are consistent with Magliano et al. (28) and Schauer and Cass (29) for winter 1995. The portions of PM_{2.5} from secondary aerosol and RWC are much lower for the non-winter (low_{PM_{2.5}}) period, while the portions due to fugitive dust and marine aerosol are larger compared to the winter period.

Evaluation of Source Contribution Estimates. Figure 3 compares the PMF MV and RWC factors with measured

source profiles. RWC samples were collected at a residential fireplace chimney burning Sierra Nevada hardwood (oak) or softwood (juniper) (39), commonly available fuels throughout the SJV. The MV samples were acquired in Las Vegas, NV during December 2003 (40) in source-dominated environments with gasoline-powered vehicles or diesel engines. Las Vegas receives California-grade fuels by pipeline from California refineries, and vehicle mixes are similar to those in California. The source samples were analyzed for the same species using the same methods as applied to the receptor samples. Contamination from road dust was removed from the MV samples by CMB using known geological source profiles (41). Figure 3 presents profiles based on two to four replicate measurements. Since both RWC and MV source profiles represent winter conditions, they are only compared with the PMF factors for the high_{PM_{2.5}} period.

The OC/EC ratio in PMF MV is 1.2, compared to 1.9 in the gasoline and 1.2 in the diesel profiles. The EC₂/EC ratio of PMF MV (0.80) is also closer to diesel (0.85) than to gasoline exhaust (0.32). The gasoline source profile contains a substantial abundance of gaseous NH₃ (2.8 times the PM_{2.5} mass), Na⁺, and K⁺, which are not as abundant in the diesel and PMF MV profiles. The PMF-derived MV profile appears to represent a combination of diesel and gasoline emissions with a dominating influence from diesel. A clear edge in the OC versus EC scatter plot (Figure 4) corresponds to the PMF MV factor, and this supports a consistent MV source profile within the SJV. Strict emissions regulation and periodic compliance testing in Nevada and California could account

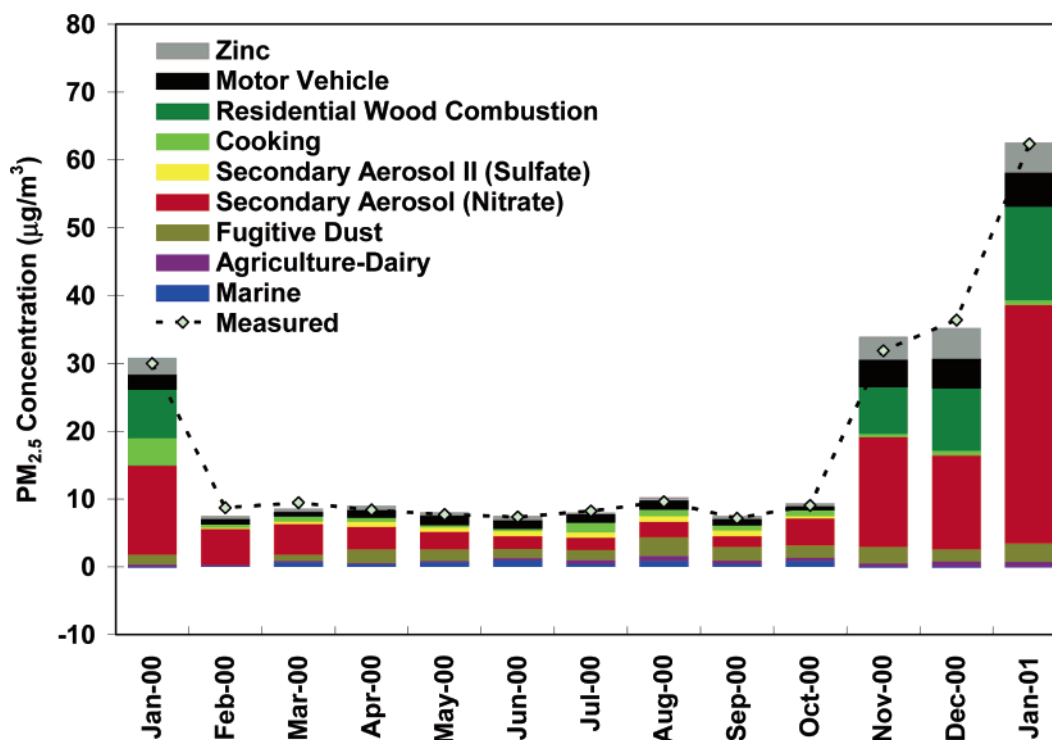


FIGURE 7. Monthly PMF factor contribution estimates averaged over the 23 CRPAQS sites.

for the low influence of gasoline engine exhaust on ambient $PM_{2.5}$. Increasing the number of factors does not distinguish the gasoline from diesel exhaust contributions. Zn is found in both diesel and gasoline profiles, possibly owing to deterioration of the galvanized exhaust systems. PMF attributed most of the Zn to a separate factor. Reducing the number of factors in PMF does not merge this factor with the MV factor.

OC/EC ratios for softwood and hardwood burning are 8.1 and 12.4, respectively, compared to 3.3 in the PMF RWC profile (Figure 4). The OC/EC ratio is known to vary with fuel and burning conditions (32). The PMF RWC factor contains more abundant NO_3^- and NH_4^+ than the measured wood burning profiles, but the T- NH_3 abundances are close. The K^+ abundance in the PMF RWC factor is comparable to that of the measured hardwood burning profile. Among carbon fractions, OC1 and POC show larger deviations between the measured profiles and PMF factors.

The PMF MV and RWC factors combined explain $10.4 \mu g/m^3$ TC or ~82% of the measured value, including 28% from MV and 54% from RWC. When the Zn factor is included, motor vehicles contribute up to 31% of TC, in better agreement with the UNMIX estimate (36% of TC).

The difference between measured and calculated species concentration divided by the measurement uncertainty, i.e., scaled residual, is a useful performance measure. Data with scaled residual >4 or <-4 are downweighted in the PMF analysis with robust mode and therefore have low impacts on the source apportionment results. For the high- $PM_{2.5}$ period, PMF determines $PM_{2.5}$ scaled residuals within ± 4 for ~80% of the data (Figure 5a). The sign and magnitude of the scaled residual vary by site, but no outlier sites or spatial trends are identified from Figure 5a. The low- $PM_{2.5}$ period, however, contains three outliers, ANGI, FSF, and BAC (Figure 5b), where PMF underestimates the $PM_{2.5}$ mass for $>60\%$ of the data. This substantial unapportioned mass implies unknown sources and/or different source profiles at these sites.

The PMF factors explain TC and NO_3^- concentrations well for the high- $PM_{2.5}$ period (see Figure S-2 in the Supporting Information); for every site, the scaled residuals are mostly within ± 4 . Broader distributions of scaled residuals for TC and NO_3^- are found during the low- $PM_{2.5}$ period. PMF underestimates TC at ANGI, FSF, and BAC, which is consistent with the situation for $PM_{2.5}$ mass. PMF also underestimates NO_3^- at FSF and BAC for the low- $PM_{2.5}$ period. PMF explains source markers such as Si, K^+ , and EC concentrations reasonably well across all sites for both periods (Figure S-2).

Adsorption of organic vapors on quartz-fiber filters that is under-corrected by blank subtraction inflates OC and TC concentrations, the ratio of OC to other species, and $PM_{2.5}$ mass closure by differing degrees (42). Better $PM_{2.5}$ mass closures (closer to 100%) are found at ANGI, FSF, and BAC during the low- $PM_{2.5}$ period (3). This partially explains why the three sites are forced into outliers in the receptor modeling that combines all sites together. Moreover, the fraction of volatilized NO_3^- was the highest at FSF and BAC during the low- $PM_{2.5}$ period (3). Variability of the organic and nitrate sampling artifacts are not part of the analytical uncertainty considered in eq 2. Source apportionment for the high- $PM_{2.5}$ period is likely more reliable, since the sampling artifacts are relatively minor compared to high ambient TC and NO_3^- concentrations.

Spatial and Temporal Variations. Figure 6 compares the PMF contributions among different sites during the high- $PM_{2.5}$ period. Similar comparisons for the low- $PM_{2.5}$ period are in the Supporting Information (Figure S-3). There is no clear spatial trend for the marine contribution during the high- $PM_{2.5}$ period, though during the low- $PM_{2.5}$ period the distribution of marine contributions is consistent with lower elevation and frequent land-sea exchange in the northern SJV.

During the high- $PM_{2.5}$ period, higher contributions from fugitive dust occurred south of FSF with the highest contribution observed at ANGI. This may be explained by the nearby unpaved road and extensive tilling and harvesting of cotton fields in the area.

Contributions from agriculture–dairy are high in some rural areas and relatively minor at urban sites such as FSF, S13, and BAC. The largest contribution in the agriculture–dairy distribution (Figure 6) represents the dairy site (FEDL), where the NH_3 concentration was at least an order of magnitude higher than at any other site. This factor would probably not appear in PMF or UNMIX if this source-oriented site was unavailable.

The RWC factor dominates at urban sites, including Fresno, Bakersfield, Modesto, Merced, Visalia, and Sacramento, and is a low contributor at non-urban sites such as ANGI. The cooking factor shows a similar spatial distribution. The urban influence of the MV factor is less than that of RWC and cooking. Even rural sites could be impacted by major highways such as I-5 and CA-99 that are major north/south arterials. Farm equipment and other non-road engines are also used throughout the SJV. Contributions of the MV factor at FSF, FREM, and FRES that are in commercial (rooftop), roadside, and residential microenvironments, respectively, in Fresno are 2.7, 4.7, and $4.8 \mu\text{g}/\text{m}^3$ $\text{PM}_{2.5}$ for the high- $\text{PM}_{2.5}$ period, compared with a more uniform RWC contribution of 24–27 $\mu\text{g}/\text{m}^3$.

Secondary aerosol contributions are highest in the southeastern SJV with little urban–rural contrast (Figure 6). This factor also contains substantial OC that is possibly of secondary origin in winter (e.g., 43). The source of factor Zn is thought to be mobile-related, though its spatial distribution is somewhat between the RWC and MV factors.

Figure 7 shows the monthly PMF factor contributions averaged over the network. The reconstructed mass agrees with the measured $\text{PM}_{2.5}$ within $\pm 10\%$ even for the low- $\text{PM}_{2.5}$ period. A rapid increase in $\text{PM}_{2.5}$ concentration from October to November results from increasing influences from RWC and secondary aerosol. These two factors also dominate the monthly highs in January 2001 (over $85 \mu\text{g}/\text{m}^3$ at FSF and BAC). Secondary aerosol is the most important factor everywhere except at FSF, where RWC was a large contributor at times during the winter. The secondary nitrate contribution decreases rapidly after January and reaches its lowest level between June and September.

Although dust contributes to no more than 20% and 5% of $\text{PM}_{2.5}$ mass for the low- and high- $\text{PM}_{2.5}$ period, respectively, it was the dominant factor in the SJV between August and September 2000 (monthly contribution: 2.7 and $2.0 \mu\text{g}/\text{m}^3$ $\text{PM}_{2.5}$, respectively). The cooking factor does not show a clear seasonal trend, but was high in January 2000. Since this factor shares three major indicators, K^+ , OC, and EC, with RWC, some overlaps of its contribution with RWC are expected during the high- $\text{PM}_{2.5}$ period. The cooking factor may be influenced by other types of burning during the low- $\text{PM}_{2.5}$ period, such as agricultural burning and forest fires. Besides K^+ , EC2 is the most influential marker for distinguishing MV from the RWC contributions. Inclusion of organic markers specific to RWC, MV, and cooking in the receptor models should improve the resolution (29, 44). This would require measurement of organic compounds on hundreds of individual samples, which is not yet practical using extractive methods, but it may be possible using thermal methods with more specific detectors (45).

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Supporting Information Available

Additional data tables and figures. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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